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GRAFTING OF LIVING POLYMERS FROM ACTIVATED POLYSILANES

by

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# GRAFTING OF LIVING POLYMERS FROM ACTIVATED POLYSILANES

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## Introduction

Polysilanes are new high molecular weight polymers with Si-Si catenation in the main chain. Although formally they resemble polyalkanes, a number of chemical and physical properties indicate strong electron delocalization in the backbone of polysilanes and show close resemblance to polyenes<sup>1,2</sup>. Thus, they conduct after doping with Lewis acids, they have remarkable photoconducting properties, they produce radicals after exposure to UV light and strong irradiation leads to complete photodegradation of polymers, after crosslinking they can be converted into ceramics. Therefore polysilanes find potential applications as excellent self-developing high contrast photoresists, as preceramic materials, as photoconductors, or initiators of radical polymerization.

Polysilanes are typically prepared from disubstituted dichlorosilanes by reductive coupling with sodium in boiling toluene. The product of this reaction has polymodal molecular weight distribution<sup>3,4</sup>. Cyclics (mostly cyclopenta- and cyclohexasilanes), low molecular weight polymer ( $M_n=5,000$ ), and high molecular weight polymer ( $M_n>100,000$ ) are formed. Several properties of polysilanes depend on the degree of polymerization (i.e. on the conjugation length)<sup>1,5</sup>. Therefore it is important to study the properties of well defined polysilanes. We were able to prepare monomodal high molecular weight poly(phenylmethylsilylenes) with low polydispersities ( $M_w/M_n<1.2$ ) using sonochemical reductive coupling at ambient temperatures<sup>6</sup>. Severe conditions of the reductive coupling with sodium allow only alkyl and aryl substituents at silicon atom. There is a need for polysilanes with different substituents to vary electronic, spectroscopic, and also mechanical and physical properties of these polymers. We described methods of the displacement of aryl groups from polysilanes<sup>7</sup>. Aryl groups could be displaced from polysilanes by strong protonic acids such as trifluoromethanesulfonic acid. The resulting triflated polysilanes are very reactive and can react not only with different nucleophiles but also can be used as active centers for the initiation of new polymer chains leading to graft (comb like) polymers. There has been a report on the initiation of the cationic polymerization of different monomers with trimethylsilyl triflate<sup>8</sup>. We have found that the initiation process for heterocyclic monomers is very slow when model silyl esters were used because the charge is mostly located on the exocyclic silyl group. Reactivity of triflated polysilanes is higher due to the

presence of  $\beta$ -Si-Si bonds and graft copolymers were prepared employing cationic polymerization and group transfer polymerization.

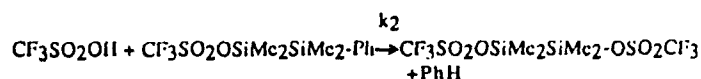
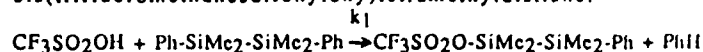
## Experimental

Poly(phenylmethylsilylene) was synthesised from phenylmethylchlorosilane and sodium dispersion prepared directly using an immersion-type ultrasonic probe (W-140, Heat Systems-Ultrasonics, Inc.)<sup>6</sup>. A toluene solution of dichlorosilane was added to the reaction flask in a controlled manner under inert gas. The reaction was quenched after the required time by using equimolar mixtures of water and ethanol. The organic phase was later added to a large excess of isopropanol leading to the precipitation of the polymer. The polymer was dried and the yield determined gravimetrically. Molecular weights and polydispersities were determined by gpc using polystyrene standards. The compositions of the polymers were measured by NMR. The dearylation experiments were carried out in argon atmosphere or by using high vacuum line technique. Cationic polymerization and grafting have been performed using vacuum line. Group transfer polymerization and grafting of poly(methyl methacrylate) onto polysilane have been carried out under inert gas with dry reagents according to the literature procedures<sup>9</sup>.

## Results and Discussion

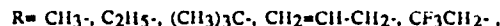
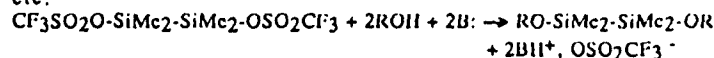
### Dearylation

Silyl esters belong to the most electrophilic reagents<sup>10</sup> and the trimethylsilyl group is considered as a "bulky proton". Trimethylsilyl iodide and trimethylsilyl triflate (trifluoromethanesulfonate) were found to be  $10^9$  times more reactive than the classical silylating reagent trimethylsilyl chloride<sup>11</sup>. Electrophilic silyl esters and halides react with a number of different nucleophiles such as alcohols, amines, ketones, esters, ethers, phosphates, etc. Usually silylation is considered to proceed via a mechanism very similar to  $S_N2$  processes. There are a few methods of incorporation of triflate groups into silanes: a reaction of silyl chloride with silver triflate or with triflic acid, or a reaction of alkyl or aryl silanes with the acid. The last reaction proceeds very rapidly and was found to be very selective for disilanes also. We found that in the reaction of 1,2-diphenyltetramethyldisilane with two equivalents of triflic acid, the disilane is quantitatively converted into 1,2-bis(trifluoromethanesulfonyloxy)tetramethyldisilane:



The rate constant of the second displacement reaction is 8 times smaller than the first one. The presence of the electron withdrawing substituent at the adjacent Si atom decreases the rate of dearylation which proceeds via protonation at the ipso C-atom in the aromatic ring. The electronic effects are transmitted very well in polysilanes due to the delocalization of the electrons in the main chain<sup>12</sup>.

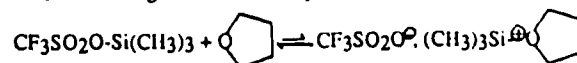
Triflated silanes and disilanes react rapidly with different nucleophilic reagents such as alcohols, amines, organometallics, etc:



The action of the triflic acid on polysilanes containing aryl groups can either lead to the cleavage of the Si-Aryl linkage or the Si-Si bond. The latter bond is cleaved easily in strained polysilanes but no Si-Si bonds are cleaved in the model disilane for which selectivity of dearylation was higher than 99%. The reaction with high molecular weight polysilanes was less selective and we found that in addition to dephenylation (95%) also polymer degradation occurred (5%). It seems that the high molecular weight polymers have a higher tendency for degradation than the low polymers for which higher selectivities were found. It may have the origin in an increase of the conjugation length with molecular weight<sup>5</sup>. For a number of possible applications a small modification (about 5%) is sufficient. At that stage dearylation is practically the exclusive reaction.

### Initiation with Silyl Triflates

Polymerization of different vinyl monomers and heterocyclics has been reported to be initiated by trimethylsilyl triflate<sup>8</sup>. We have done some detailed studies of the initiation of THF polymerization in different solvents and under conditions at which no propagation was possible. The equilibrium of the silylation reaction was shifted towards the substrates in media of low and medium polarity. This indicates that the charge in the hypothetical trimethylsilyltetrahydrofuranium cation is mostly located on the silyl moiety which is then attacked by the triflate anion forming back the silyl triflate:

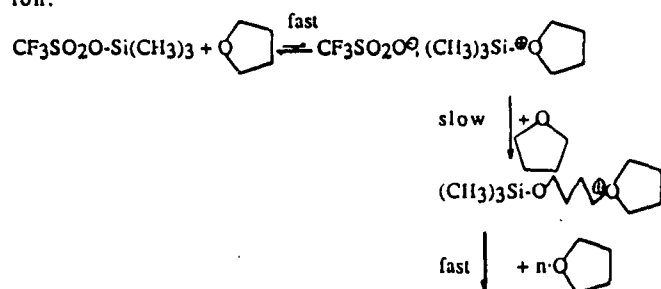


The approximate calculations by MNDO methods show that in the trimethylsilyltetrahydrofuranium cation the positive charge is located mostly on silicon atom (81.7%), contrary to the methyltetrahydrofuranium cation in which there is only small excess of the positive charge on the exocyclic  $\alpha$ -C atom in comparison with the endocyclic C atoms. The charge on the endocyclic  $\alpha$ -C atoms increases from 15.3% for uncharged THF, to

15.7% for trimethylsilylated ring and to 18.5% for methylated ring. This is in good agreement with the  $^1\text{H}$  NMR chemical shifts of  $\alpha$ -methylene protons (3.63, 3.77, and 4.92 ppm respectively) in  $\text{CD}_3\text{NO}_2$  solvent. Polymerization of THF in polar solvents proceeds predominantly via ionic active species<sup>13</sup>.

The experimental results as well as the approximate calculations show that initiation in this system must be slow because of the weakly charged  $\alpha$ -endocyclic C atoms.

Polymerization of THF by trimethylsilyl triflate leads to polymers with higher molecular weights than predicted from the ratio of the reacted monomer to trimethylsilyl triflate and is accompanied by induction periods. Although the first silylation reaction could be quite rapid (only one NMR signal of free and silylated THF), the initiation process is slow due to low reactivity of the  $\alpha$ -endocyclic C atoms in trimethylsilyltetrahydrofuranium ion:



Traces of moisture hydrolyze trimethylsilyl triflate to form triflic acid (potential initiator) and hexamethyldisiloxane. The latter product was indeed observed in the reaction mixtures. Initiation by protonic acid could be completely suppressed by the hindered pyridine which reacts irreversibly with acids and does not react with more bulky electrophilic species such as trimethylsilyl ester or tetrahydrofuranium cation.

#### Grafting from Polysilanes via Cationic Polymerization

Solutions of polysilanes of low and high molecular weights were treated with controlled amounts of triflic acid in  $\text{CH}_2\text{Cl}_2$  and subsequently allow to react with THF. Solutions of hindered pyridine (2,6-di-*t*-butyl-4-methylpyridine) were added in some experiments to prevent the polymerization by traces of triflic acid which could be present in the reaction mixture. A strong increase in the viscosities was found after a few hours. The resulting high polymers precipitated from methanol absorbed strongly in UV above 300nm indicated the content of polysilane backbone. Increase of molecular weights from  $M_n=3,000$  (polysilane) to  $M_n=81,000$  (graft copolymer) was observed. Absorbance of high polymer above 300 nm in UV indicates a graft structure. Poly(tetrahydrofuran)-*g*-poly(phenylmethylsilylene) was photodegraded by UV lamp. A decrease in the molecular weights from  $M_n=81,000$  to  $M_n=34,000$  was observed. This result indicates the presence of the average 2.4 active sites per initial polysilane chain. Under identical conditions no degradation of homopolyTHF was found.

Similar reactions performed with other vinyl and heterocyclic monomers using not only triflated polysilanes, but also halogenated polysilanes will be discussed later.

#### Grafting from Polysilanes by Group Transfer Polymerization

Silyl triflates are very powerful silylating agents and they can react directly with alkyl esters to form the corresponding silyl ketene acetals. Amines and pyridines are used in order to

trap triflic acid which is formed under these conditions. We prepared initiators in situ from trimethylsilyl triflate (or aryl silanes and equimolar amounts of triflic acid), methyl propionate, and triethyl amine. Tris(dimethylamino)sulfonium)hexafluoride was used as catalyst. Polymers with higher than theoretical molecular weights were formed under these conditions. This can have the origin in lower activity of silyl ketene acetals based on propionate rather than isobutyrate esters which have higher "O/C" silylation ratios. Similar reaction was applied for poly(phenylmethylsilylene) ( $M_n=3,000$ ) as the silylating reagent. In this case poly(methyl methacrylate)-*g*-poly(phenylmethylsilylene) was formed. The graft copolymer was degraded by UV light from  $M_n=125,000$  to  $M_n=47,000$  in 24 hrs. No further degradation was observed at longer irradiation time. Three pMMA branches per polysilane chain were expected from the [Polysilane]*g*/[MMA]*n* ratio. Degradation indicates that each polysilane chain contains 2.7 pMMA grafts which suggests that not all triflated sites were active.

Poly(methyl methacrylate) prepared in this experiment as well as polymers formed in model reactions with silanes having bulky substituents such as phenyldimethyl and diphenylmethyl have predominantly syndiotactic structure identical to polymers prepared in the conventional group transfer process. This result favors two-step dissociative mechanism of GTP because steric hindrances from bulky silyl groups should increase proportion of isotactic triads in the hypothetical associative concerted process.

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Table 1

Charge Distribution (by MNDO) on the  $\alpha$ -Endocyclic C-atoms in Tetrahydrofuranium Cations and  $^1\text{H}$  NMR Chemical Shifts of the Corresponding Methylene Protons

	% of Charge	% of Charge (+) on the	$^1\text{H}$ NMR
	on the Ring	$\alpha$ -Endocyclic C-atoms	
	0	15.3	3.63
	68	16.5	3.9
	59	18.5	4.92
	54	17.8	-
	34	15.7	3.77